

**IN THE SPECIFICATION:**

Please amend paragraphs [0005], [0007], [0021], [0022], [0025], [0028], [0029], [0030], [0031], [0033], [0034], [0035], and [0036], and add new paragraphs [0020.1] and [0020.2], as follows:

[0005]        Figure 1 is a conventional plating apparatus. Conventional electroplating methods generally include positioning a substrate 101 on a substrate support member 102 in a face down configuration, *i.e.*, the receiving surface 103 of the substrate support member secures the substrate 101 thereto such that the exposed surface of the substrate faces downward, as illustrated in Figure 1. The substrate support member 102 is then lowered into a plating bath 104, which generally comprises an electrolytic solution. An electrical bias is then applied between the surface of the substrate and an anode positioned in the plating bath, which operates to urge metal ions in the plating solution, which may be copper ions, to deposit on the substrate surface. During non-processing time periods, *i.e.*, when substrates are not being plated, the electrolytic solution is generally circulated through a continual path that includes a relatively small volume plating bath/cell 104 and a substantially larger volume storage cell 105. The storage cell 105, for example, may hold approximately 200 liters of plating solution, while the plating cell 104 may hold approximately 2 liters of plating solution. Additionally, the continual fluid path may include an electrolyte replenishment device 106 configured to replenish portions of the plating solution that may be depleted through plating operations.

[0007]        During the plating process, copper ions are continually being removed and replenished to/from the electrolytic solution, and therefore, the copper concentration of the electrolyte inherently changes or varies over time. This concentration change may further be affected by volume depletion of the plating solution and/or dissolution of the anode. Additionally, plating operations also deplete the various organic molecules in the electrolyte solution, and therefore, the organic concentration also varies over time. For example, levelers are known to deplete/breakdown upon exposure to oxygen

containing elements, *i.e.*, ambient air, oxygen absorbed into the plating solution, oxygen molecules contained in the anode metal, or oxidation encountered during plating by incorporation into a growing film. This breakdown process generates free radicals in the plating solution, which are undesirable, as the free radicals can deposit on a substrate and contaminate the metal layer. Further, levelers are known to breakdown upon exposure to copper, copper alloys, and/or platinum, all of which are typical anode materials for electroplating systems. Similarly, accelerators and suppressors may also suffer from depletion/breakdown characteristics as a result of oxygen and/or metal exposure. Depletion of organics is not limited to processing time periods, as the electrolyte solution in electroplating systems is generally continually circulated through the plating cell, storage unit, and potentially a replenishment device during non-processing time periods. As a result of the circulation, the plating solution may be continually exposed to both oxygen-containing elements and the metal anode. Therefore, as a result of this exposure, the organic molecules in the plating solution are continually being depleted, ~~eventhough~~ even though the plating system is not in a plating or operational mode.

[0020.1] Figure 6 illustrates a sectional view of the exemplary substrate support assembly illustrated in Figure 5.

[0020.2] Figure 7 illustrates an exemplary depletion determination and processing recipe modification method of the invention.

[0021] Figure 2 is a perspective view of an exemplary electroplating system platform 200 of the invention. Figure 3 is a schematic plan view of the exemplary electroplating system platform 200 of the invention. Referring cooperatively to Figures 2 and 3, the electroplating system platform 200 generally includes a loading station 210, a thermal anneal chamber 211, a spin-rinse-dry (SRD) station 212, a mainframe 214, and an electrolyte replenishing system 220. The mainframe 214 generally includes a ~~mainframe transfer station 216~~ having a plurality of processing stations 218. Each processing station 218 may include one or more processing cells 240. An electrolyte

replenishing system 220 is generally positioned adjacent the electroplating system platform 200 and individually in fluid communication with each of process cells 240 in order to circulate fresh electrolyte thereto that will be used for the electroplating process. The electroplating system platform 200 may also include a control system 222, which may be a programmable microprocessor-type controller configured to interface with the various components of system platform 200 and provide controlling signals thereto. Control system 222, for example may be used to control parameters associated with the plating process, such as electrical bias applied to a substrate, duration of substrate exposure to electrolyte solutions, rotation rates of substrate support members, flow rates of electrolyte into plating cells, flow rates of organic molecules into the plating solution via the replenishment module 220, actuation of valves related to the plating process, *i.e.*, check valves and bleed valves, along with other parameters generally associated with the execution of the semiconductor processing recipe in a plating apparatus. Loading station 210 generally includes one or more substrate cassette receiving areas 224, one or more loading station transfer robots 228, and at least one substrate orientor 230. The number of substrate cassette receiving areas 224, loading station transfer robots 228, and substrate orientors 230 included in the loading station 210 may be configured according to the desired throughput requirements of the particular system.

[0022] Figure 4 is a cross sectional view of an exemplary electroplating process cell 400 of the invention. The electroplating process cell 400, for example, may be implemented into the process cell location 240 illustrated in Figure 3. Process cell 400 generally includes a head assembly 410, a process kit 420, and an electrolyte collector 440. Preferably, the electrolyte collector 440 is secured onto the body 442 of the mainframe 414 over an opening 443 that defines the location for placement of the process kit 420. The electrolyte collector 440 includes an inner wall 446, an outer wall 448, and a bottom 447 connecting the respective walls. An electrolyte outlet/overflow 449 may be disposed through the bottom 447 of the electrolyte collector 440 and connected to an electrolyte replenishing system 480 through tubes, hoses, pipes, or other fluid transfer connectors. The outer wall 421 of process kit 420 defines an open

top enclosure 475 configured to contain ~~and~~ an electrolytic plating solution therein. Enclosure 475 includes an electrolyte supply line 476 that is generally in communication with an electrolyte supply or storage unit and includes a check valve 477, which may generally operate to selectively terminate electrolyte flow-through supply line 476. Supply line 476 is generally configured to supply electrolyte from a storage container to the processing enclosure 475. Enclosure 475 may further include an electrolyte bleed line 478, which may be in fluid communication with enclosure 475 and positioned vertically within the outer wall 421 of enclosure 475 at a level just above an upper surface of an anode 470 positioned within enclosure 475. Bleed line 478 may include a selectively actuated valve 479, which may be used to initiate bleed line flow of electrolyte out of enclosure 475. Bleed line 478 may be in fluid communication with a fluid drain, or alternatively, bleed line 478 may be in communication with the storage/replenishment device mentioned above.

[0025] A depletion rate determination process generally includes executing at least one test run of the plating system to determine the depletion rate of specific organic molecules from the plating solution as a function of the current density applied in the plating process. For example, in a plating system where the current density applied during plating operations is generally between  $10 \text{ A/cm}^2$  and  $15 \text{ A/cm}^2$ , the test run process may include an incremental test of current densities between 10 and 15  $\text{A/cm}^2$ . This type of test run process, for example, may include plating a substrate at  $10 \text{ A/cm}^2$  for a predetermined period of time, and then measuring the depletion of organic molecules from the electrolyte solution at the end of the predetermined period of time. Once the depletion of organics for the tested current density is measured/known for the given current density over the predetermined unit of time, the depletion of the organics per individual unit of time for the given current density may be determined through calculation, assuming that the initial or starting organic concentration is known before the test run process is commenced. The calculation process, for example, may determine an organic concentration differential, *i.e.*, the difference between the organic concentration before the test run and the organic concentration after the test run, and then use the concentration differential to determine the volumetric depletion of organics

during the test run process. Once the volumetric depletion is determined, it may be divided by the test run duration to determine the volumetric depletion per unit of time. Therefore, for example, if a test run measurement of plating at  $10 \text{ A/cm}^2$  for 20 units of time determines that 40 volumetric units of a specific organic molecule (organic "A") are depleted during the 20 units of time, then it may be determined/calculated that the depletion of organic A per unit of time for a current density of  $10 \text{ A/cm}^2$  is 2 volumetric units per unit of time. This test, measure, and calculate process may then be incrementally repeated for various current densities within the range of normal operation of the particular plating system. For the exemplary system noted above that generally operates in the  $10 \text{ A/cm}^2$  to  $15 \text{ A/cm}^2$  range, test runs may be executed at  $11 \text{ A/cm}^2$ ,  $12 \text{ A/cm}^2$ ,  $13 \text{ A/cm}^2$ ,  $14 \text{ A/cm}^2$ , and  $15 \text{ A/cm}^2$ , for example, wherein each test run may be conducted for a predetermined time interval.

[0028] Using a current density of  $10 \text{ A/cm}^2$  as an example, the plating system may be run with the current density of  $10 \text{ A/cm}^2$  for 20 units of time. Once the  $10 \text{ A/cm}^2$  test run is complete, the plating solution in the plating system may be measured to determine the remaining concentration of organics in the plating solution. Using the measured organic concentration, the volumetric depletion of the organics may be determined. For example, in the  $10 \text{ A/cm}^2$  test run, it may be determined that 40 volume units of organics were depleted from the solution during the 20 units of time of the test run. Therefore, using this information, the method of the invention may then calculate the volumetric depletion of organics per unit time for a current density of  $10 \text{ A/cm}^2$ , which is illustrated as 2 volumetric units of organics depleted per unit of time (40 volumetric units depleted divided by 20 units of time yields 2 volumetric units depleted per individual unit of time). This process may then be repeated for various other current densities. In the exemplary method illustrated in Figure 7, the current density test runs are repeated for current densities of 11, 12, 13, 14, and  $15 \text{ A/cm}^2$ , each using a time duration of 20 units of time. However, although 20 units of time are illustrated for each current density test run in the exemplary method illustrated in Figure 7, it is not necessary or required for the test run time duration to be identical for each test run. Rather, the time duration may be varied per current density test run in order to increase

the efficiency of the individual run, *i.e.*, if depletion for a particular current density may be accurately measured in a shorter time duration, then the time duration may be shortened. Similarly, if a particular current density requires a longer test run duration in order to obtain an accurate depletion measurement, the time duration may be lengthened to accommodate an accurate measurement.

[0029] Additionally, although current densities of 10 to 15 A/cm<sup>2</sup> are illustrated in the exemplary method of Figure 7, the invention is in no way limited to these current densities. Rather, it is contemplated that the method of the present invention may be applied to a wide range of current densities. It is to be noted, however, that generally the range of current densities implemented in the test runs will be determined by the normal operational current density range of a plating process or apparatus. For example, if a particular plating operation or apparatus generally operates using current densities in the range of 35 to 55 A/cm<sup>2</sup>, then the test runs may be adjusted to incorporate this current density range. Similarly, if the normal operation range for a plating system uses current densities between 2 A/cm<sup>2</sup> and 2.2 A/cm<sup>2</sup>, then the test runs may be conducted at 2, 2.05, 2.10, 2.15, and ~~2.2 A/cm<sup>2</sup>~~, for example 2.2 A/cm<sup>2</sup>, for example. Therefore, generally speaking, the range of current densities utilized in the test runs may be determined by the normal operational current density range used in the plating process of a particular processing recipe or plating apparatus, regardless of the magnitude of the current density.

[0030] Once the test run process is complete, the method of the invention generally includes calculating the volumetric depletion of organics per unit of time for each current density implemented in the test runs, as illustrated in step 2 of Figure 7. This calculation, which is briefly discussed above, generally includes determining the volumetric depletion of the concentration of organics in the plating solution during the individual test runs. Once the volumetric depletion of organics is determined, the volumetric depletion may be divided by the time duration of the test run at the particular current density in order to yield the volumetric depletion of organic material per unit of time for the respective current density. As illustrated Figure 7, for example, for the 14

A/cm<sup>2</sup> current density test run, it may be determined from the concentration change of organics in the plating solution that the volumetric depletion of organics from the plating solution is 40 50 volume units. The volumetric depletion may then be divided by the time duration of the test run to determine the volumetric organic depletion per unit time. For example, for the 14 A/cm<sup>2</sup> test run it was determined that 45 50 volume units of organics were depleted from the plating solution over 20 units of time. Therefore, dividing 45 50 volume units by 20 units of time yields an organic volumetric depletion per unit time of 2.5. The calculation of the volumetric depletion per unit time may be repeated for each individual current density used in the test run process. As such, the volumetric depletion per unit time may be calculated for each current density that may be used in the operation of the plating system.

[0031] Once the volumetric depletion per unit time is determined for the respective current densities used in the plating system, *i.e.*, for each test run, then a processing recipe implemented in the plating system may then be modified and/or adjusted to include real-time replenishment of the depleted organics during the plating process. For example, as illustrated in step 3 of Figure 7, an exemplary processing recipe having four individual recipe steps therein (A, B, C, and D ~~and E~~) may be modified to include real-time replenishment of depleted organics within the individual recipe steps. Within recipe step A, for example, it may be determined from the test run that using a current density of 10 A/cm<sup>2</sup> requires organic replenishment of 2 volumetric units of organics per unit time. Therefore, during the five units of time of recipe step A, organics may be replenished into the plating solution at a rate of 2 volumetric units of organics per unit of time, as step A operates at 10 A/cm<sup>2</sup>, and this current density has been found to deplete 2 volumetric units of organics per unit of time in the test run process. Therefore, although the plating operation is depleting organics at a rate of 2 volumetric units per unit of time, the present invention is simultaneously replenishing 2 volumetric units of organics into the plating solution during the plating process. Therefore, the resulting organic depletion rate in the plating solution is nullified, as the organics being depleted from the solution are simultaneously being replaced by a replenishment process. Further, the organic concentration gradient may be minimized,

as the concentration of organics generally will not vary using the present invention. The replenishment process may continue through the remaining recipe steps (B, C, and D) in a similar manner to that described for step A. For example, during the 10 units of time of recipe step B, 25 volumetric units of organics may be replenished into the plating solution, as it was calculated from the test run that 2.5 volumetric units of organics are depleted per unit time from the plating solution while the plating process is operating at a current density of 14 A/cm<sup>2</sup>. Similarly, during recipe steps C and D, 11.5 and 10 volumetric units may be replenished into the plating solution, respectively.

[0033] Additionally, the microprocessor-type controller may also be used to ~~extrapolate~~ interpolate data between test run current densities. For example, if test runs having current densities of 15 A/cm<sup>2</sup> and 17 A/cm<sup>2</sup> are run, and a processing recipe step utilizes a current density of 16 A/cm<sup>2</sup>, then the microprocessor type controller may be used to ~~extrapolate~~ interpolate the appropriate volumetric replenishment of organics for the current density of 16 A/cm<sup>2</sup>. The ~~extrapolation~~ interpolation process may, for example, use a weighted average's method to determine volumetric depletion rates for current densities not specifically tested in the test run process.

[0034] In another embodiment of the invention, depletion of organics during non-processing time periods may be minimized. For example, ~~as illustrated Figure 8,~~ a method for reducing depletion of organics during non-processing time periods may include the steps of isolating the processing cell 804 and draining the process cell 802. The isolation step 804 generally includes closing a check valve positioned in the electrolyte supply line, *i.e.*, in the line supplying fresh electrolyte to the processing cell for processing. For example, referring to the exemplary plating apparatus 400 illustrated in Figure 4, check valve 477 may be closed in order to terminate the flow of fresh electrolyte into processing region 475 during non-processing time periods. Therefore, with check valve 477 closed, processing region 475 is generally isolated. Once processing region 475 is isolated, a substantial portion of the remaining electrolyte solution contained within processing region 475 may be drained therefrom. For example, again referring to the plating apparatus 400 illustrated in Figure 4, a



substantial portion of the electrolyte solution contained in processing region 475 may be removed therefrom by bleed line 478. The removal process generally includes opening a bleed valve 479 such that the electrolyte solution contained within processing region 475 may be allowed to flow out bleed line 478. Bleed line 478 may be in communication with a fluid drain, an electrolyte replenishment device, or an electrolyte storage cell, for example. Assuming bleed line 478 is positioned in the sidewall 421 of processing region 475 just above anode 470, within bleed line 478 may operate to remove a substantial portion of the electrolyte solution from processing region 475, while leaving enough electrolyte solution to maintain the anode 470 in solution. Therefore, assuming the volume of processing region 475 is approximately two liters, bleed line 478 may be used to remove approximately 1 to 1 1/2 liters of electrolyte solution therefrom. When a substantial portion of the electrolyte solution contained within processing region 475 has been removed, then bleed valve 479 may be closed to again isolated processing region 475. Alternatively, if anode 470 does not need to be maintained in solution, then bleed line 478 may be positioned in the bottom of the electrolyte container so that substantially all of the electrolyte may be drained from the electrolyte container during non-processing time periods.

[0035] With a substantial portion of the electrolyte solution removed from processing region 475, and with processing region 475 isolated from the remaining volume of electrolyte solution in the plating system, the depletion of organics during the non-processing time period is minimized. The minimized depletion of the organics is a result of the electrolyte solution neither flowing over the anode 470 nor contacting oxygen containing elements. Rather, the bulk of the electrolyte solution is maintained in an electrolyte storage container positioned proximate the plating apparatus 400 and is not continually circulated through the plating cell 475. Inasmuch as electrolyte circulation during non-processing time periods results in a substantial portion of the electrolyte depletion during non-processing time periods, electrolyte depletion is minimized by the isolation and draining method of the present invention.

[0036] Once the non-processing time period is over, plating apparatus 400 may be returned to a processing mode. The transformation from the non processing time period to a processing mode may generally include a starter or initialization phase. For example, the starter or initialization phase may be configured to refill the processing region 475 with fresh electrolyte prior to commencing plating operations. As such, the initialization phase may include opening of check valve 477, such that fresh electrolyte may begin to flow into and fill up processing region 475. The filling process may include leaving bleed line 479 open, such that fresh electrolyte may be allowed to flush processing region 475, i.e., fresh electrolyte may be pumped into processing region 475 by fluid supply line 476, while electrolyte is simultaneously being removed from processing region 475 by bleed line 478. As such, processing region 475 is flushed of the portion of electrolyte that remained therein during the non-processing time period, i.e., the old electrolyte that was used to maintain the anode immersed in fluid during the non processing time period may be removed. Once processing region 475 is flushed of ~~to~~ the old electrolyte, bleed valve 479 may be closed, and therefore, processing region 475 may be supplied with fresh electrolyte from supply line 476 for normal plating operations. Alternatively, another bleed line may also be positioned in a lower portion of processing region 475, and therefore, this additional bleed line may be used to simply dumped the old electrolyte from processing region 475 during the initialization process in this embodiment, once the old electrolyte is dumped from processing region ~~4 to 75~~ 475, check valve 477 may be opened in fresh electrolyte supplied to processing region 475 via fluid supply line 476.

**IN THE DRAWINGS:**

The attached sheets of drawings include changes to Figures 2, 3, 4, 5, and 6. These sheets, which include Figures 2, 3, 4, 5, and 6, replace the original sheets including Figures 2, 3, 4, 5, and 6.

In Figure 2, previously omitted elements 218 and 224 have been added, and an arrow pointing to element 211 has been added.

In Figure 3, reference numbers 100, 110, 111, 112, 114, 118, 120, 122, 124, 128, 130, and 140 have been amended, and reference numbers 132, 134, and 138 have been deleted.

In Figure 4, previously omitted reference number 421 has been added, and extraneous reference numbers 450, 452, 454, 456, 457, 458, 462, 464, 466, 467, and 468 have been deleted.

In Figure 5, the reference number for previously mislabeled element 505 has been deleted, and extraneous reference numbers 503 and 504 have been deleted.

In Figure 6, the reference number for previously ambiguously labeled element 508 has been relocated to more clearly point out that element, omitted reference numbers for elements 510 and 511 have been added, and extraneous reference numbers 502, 503, 504, and 509 have been deleted.

**Attachments:**      Replacement Sheets  
                         Annotated Sheets Showing Changes